

PATENT ABSTRACTS OF JAPAN

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(54) METHOD FOR PREPARING SUB-STOICHIOMETRIC OR STOICHIOMETRIC NITRIC ACID SALT SOLUTION

(57)Abstract:

PURPOSE: To provide a method for preparing a sub-stoichiometric or a stoichiometric nitric acid salt solution of a nuclear fuel, etc., used for a starting material in preparing fine small spherical ceramic particles of ceramic fuel particles, etc., for a nuclear reactor.

CONSTITUTION: This method for preparing a sub-stoichiometric or a stoichiometric nitric acid salt solution comprises taking a solution or a solid of the stoichiometric metal nitric acid salt in which the concentration ratio of nitric acid/the metal (hereinafter, called a nitric acid concentration ratio) is equal to the metal or its complex cationic valence number (hereinafter, called a metal-containing cationic valence number) as a starting material and in order to obtain the solutions of sub-stoichiometric nitric acid salt or stoichiometric nitric acid salt, where the nitric acid concentration ratio is smaller than the metal-containing cationic valence number, while heating the solution or the solid of the starting material in a air stream containing water vapor, capturing the discharged nitric acid in the alkaline solution of a knot amount, and stopping the reaction at the time of getting the objective discharged amount. In this way, the sub-stoichiometric or stoichiometric nitric acid salt solution having the objective nitric acid concentration ratios are prepared.

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CLAIMS

[Claim(s)]

[Claim 1] A nitric acid / metal ratio of concentration (it is hereafter described as the nitric-acid ratio of concentration) A metal or its compound cation valence The solution or solid-state with which the isolation nitric acid joined the solution of a stoichiometric metal nitrate equal to (calling it a metal content cation valence hereafter), a solid-state, or it is used as starting material. In order that the nitric-acid ratio of concentration may obtain the solution of a ***** nitrate smaller than a metal content cation valence or a stoichiometric nitrate How to prepare ***** or the stoichiometric nitrate solution of the nitric-acid ratio of concentration made into the purpose by stopping a reaction when uptake of the nitric acid emitted heating the solution or solid-state of starting material in the air current containing a steam is carried out into the ant potash solution of a known amount and a target burst size is reached.

[Claim 2] ***** or the stoichiometric nitrate solution preparation approach of claim 1 that whenever [stoving temperature] is 190 degrees C or less.

[Claim 3] ***** or the stoichiometric nitrate solution preparation approach of claim 1 by adding water, where the heated matter after a reaction termination is maintained at 80-99 degrees C, and dissolving all solid-states.

[Claim 4] ***** or the stoichiometric nitrate solution preparation approach of claim 1 that the nitric-acid ratio of concentration is 75 - 100% of range of a metal content cation valence.

[Claim 5] ***** or the stoichiometric nitrate solution preparation approach of claim 1 which is one selected sort or the selected nuclear fuel material beyond it to which this metal changes from the group of uranium, thorium, and a transuranic element.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the preparation approach of ***** such as a nuclear fuel material used as starting material in the case of preparing minute spherical ceramic particles, such as a ceramic fuel particle for reactors, or a stoichiometric nitrate solution.

[0002]

[Description of the Prior Art] In the production process of the fuel gel particle by the sol gel process used in the field of the ceramic fuel particle for reactors, when preparing the ***** nitrate solution containing fuel metals, such as uranium which is a starting material solution, the approach of dissolving metallic-oxide powder in a nitric acid or a stoichiometric metal nitrate solution, or adding an organic substance reducing agent to a stoichiometric nitrate solution, and disassembling and removing a nitric acid is taken.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the approach of preparing the target starting material solution, without passing through the handling process of the fuel oxide impalpable powder which is the radioactive substance which brings about indispensable increase of a worker exposure with the conventional technique, or the process accompanied by risk of adding an organic substance reducing agent in the nitrate solution which is an oxidizer.

[0004]

[Means for Solving the Problem and its Function] The means adopted for the technical-problem solution solve it the purpose as a result of wholeheartedly research of an invention-in-this-application person is as follows.

[0005] The 1st is having raised denitrification acid effectiveness, and also the principal component of emission gas being made to the form of a nitric acid rather than nitrogen oxides, and having enabled it to control the terminal point of the denitrification acid reaction of the purpose automatically correctly as follows with heating in the ambient atmosphere containing a steam. That is, it leads into the water 3 which heated support gas 1 at the heater 2 using equipment as shows an example to drawing 1, and a steam is included, and it lets the incubation furnace 4 pass, and leads in the nitrate container 6 heated at the heater 5. The nitric acid which this emitted is led into the alkali solution 9 for nitric-acid uptake through the condensator 7 which is not pouring cooling water, and the condensator 8 which is pouring cooling water continuously with support gas. Let the original amount of alkali in this solution be the nitric acid and the equivalent which should be made to emit. In order to stop emission system outside of a generating nitric acid, the solenoid operated directional control valve 13 for pouring cooling water 12 also to a condensator 7 is operated at the same time it stops heating at the terminal point [solution / an emission nitric acid and / alkali] of neutralization according to a heater 5 by the signal of rapid pH change, acting as the continuation monitor of the pH of this alkali solution with the recording controller 11 connected with the pH meter 10.

[0006] If the heated object of the shape of fused salt in the container 6 after reaction termination is cooled and solidified to a room temperature, since container breakage will arise by the cubical expansion by moisture absorption of the solid-state, the 2nd is cooling, after opening a hand valve 14 in the condition of having maintained to the elevated temperature 100 degrees C or less which is the boiling point of water, adding Nakamizu of a sump 15 and changing a solid-state into a water solution, in order to prevent it.

[0007]

[Example] This invention is concretely explained about an example. However, this invention is not limited by the example.

[0008]

[Example 1] Aging of the NO₃-/U mole ratio in a sample was investigated by the approach of investigating the amount of emission nitric acids while sometimes exchanging supply and the sodium-carbonate solution for emission nitric-acid uptake for a sample for the mixed gas (steam + argon) which carried out the bubble of the argon the rate for 50m1/into the 95-degree C water of a steam generator, using an oil bath as a heating heater of the sample (uranyl-nitrate solution) of the equipment of drawing 1. The sample before a reaction is 1.60m of isolation nitric-acid content uranyl-nitrate solutions whose NO₃-/U mole ratio U concentration is 2.10 in 1/1 2.00 moes.

[0009] Sample temperature became about 110 degrees C in about 80 minutes after heating initiation of an oil bath with a laying temperature of 160 degrees C, emission of a nitric acid started, and the NO₃-/U mole ratio amounted to 1.86 as a result of heating by 430 minutes. (The calculated value from an uptake nitric acid was in agreement in

the range with error by 1.83) . Sample temperature was after 290 minute 147 degrees C. Sample temperature in the meantime and the NO₃-/U mole ratio of the sample calculated from the uptake nitric acid are shown in drawing 2 to the time amount after heating initiation. (The result at the time of supplying only argon gas is also compared and shown in drawing 2 .)

[0010]

[Example 2] By the same technique as an example 1, only oil bath laying temperature was changed into 195 degrees C, and aging of a NO₃-/U mole ratio was investigated. After [of an after / heating initiation] 206 minutes, the NO₃-/U mole ratio amounted to 1.63. (The calculated value from an uptake nitric acid was in agreement in the range with error by 1.65) . Sample temperature was after 130 minute 180 degrees C. Sample temperature in the meantime and the NO₃-/U mole ratio of the sample calculated from the uptake nitric acid are shown in drawing 3 to the time amount after heating initiation. (The result at the time of supplying only argon gas is also compared and shown in drawing 3 .)

[0011]

[Example 3] Using the equipment shown in drawing 1 , the same front [heating] sample as an example 2 and heating conditions were applied, and it experimented in the desired value of a NO₃-/U mole ratio as 1.55. When an emission nitric acid until the final value of the NO₃-/U mole ratio of a sample amounts to 1.55, and the sodium carbonate of the equivalent were specifically included in the alkali solution for emission nitric-acid uptake and pH of the solution amounted to 4, it set up so that the signal of the solenoid-operated-directional-control-valve 13 actuation which supplies cooling water to the power off and the condensator 7 of the sample heating heater 5 might be taken out.

[0012] Sample temperature was after 160 minute 184 degrees C. pH became below the set point after 252 minutes, and said signal was emitted. When sample temperature became 80 degrees C after heating termination, the hand valve 14 was opened and predetermined water was supplied in the specimen container from the sump 15. In order to dissolve all internal solid-states, finally it heated at 95 degrees C. The NO₃-/U mole ratio of this sample solution was 1.57 which is in agreement in the range of desired value and an error.

[0013]

[Effect of the Invention] The process which deals with the radioactive impalpable powder which causes increase of worker exposure extent, or the high reduction reaction process of danger was required of the Prior art. However, these processes were made unnecessary as a result of this invention, and also denitrification acidity realized the preparation approach of possible ***** of automation, or a stoichiometric nitrate solution controllable as the target. Moreover, the approach of progressing at effectiveness higher than what is depended on a pyrolysis so that it may be shown as compared with drawing 2 and 3 was realized by performing a denitrification acid reaction in a steam.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown an example of the equipment for enforcing the approach of this invention.

[Drawing 2] It is the graph which showed the sample temperature in the case of the example 1 using 160-degree-C oil bath as a sample heating heater, and aging of the NO₃-/U mole ratio in a sample as compared with the case where only argon gas is supplied.

[Drawing 3] It is the graph which showed the sample temperature in the case of the example 2 using 195-degree-C oil bath as a sample heating heater, and aging of the NO₃-/U mole ratio in a sample as compared with the case where only argon gas is supplied.

[Description of Notations]

- 1: Support gas
- 2: Heater
- 3: Steam generator
- 4: Incubation furnace
- 5: Heater
- 6: Nitrate container
- 7: Condensator
- 8: Condensator
- 9: Alkali solution
- 10: PH meter
- 11: Recording controller
- 12: Cooling water
- 13: Solenoid operated directional control valve
- 14: Hand valve
- 15: Sump

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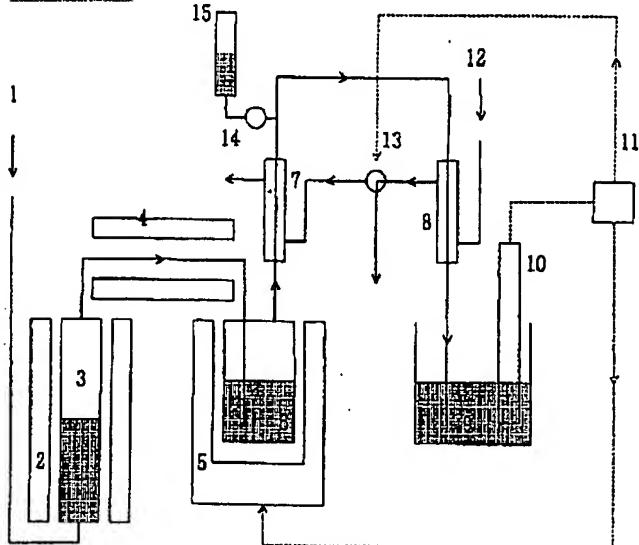
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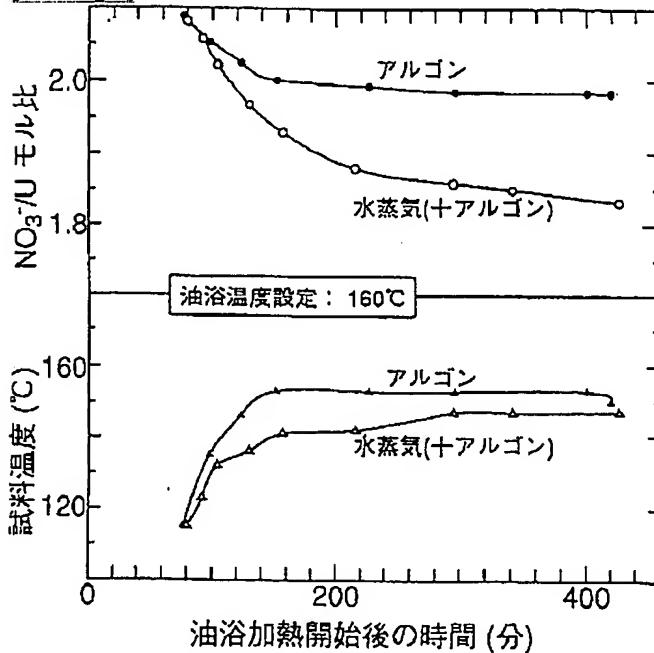
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DRAWINGS

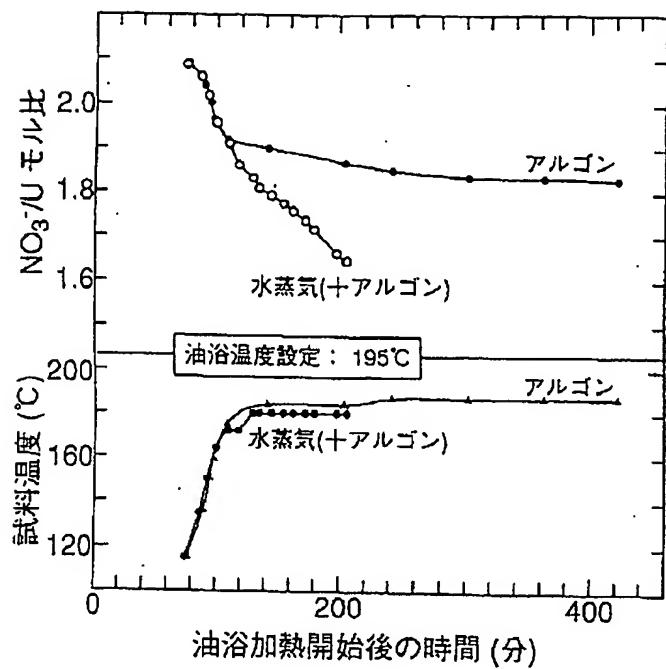
[Drawing 1]



[Drawing 2]



[Drawing 3]



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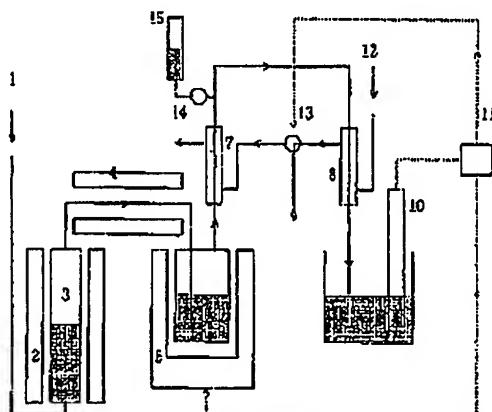
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(54)【発明の名称】 亜化学量論的または化学量論的硝酸塩溶液調製方法

(57)【要約】

【目的】 原子炉用セラミックス燃料粒子等の微小球状セラミックス粒子を調製する場合の出発物質として使用される核燃料物質等の亜化学量論的または化学量論的硝酸塩溶液の調製方法

【構成】 硝酸/金属濃度比(以下、硝酸濃度比と記す)が金属またはその複合陽イオン価数(以下、金属含有陽イオン価数という)に等しい化学量論的金属硝酸塩の溶液または固体、あるいはそれに亜硝酸硝酸が加わった溶液または固体を出発物質として、硝酸濃度比が金属含有陽イオン価数より小さい亜化学量論的硝酸塩または化学量論的硝酸塩の溶液を得るために、出発物質の溶液または固体を水蒸気を含む気流中で加熱しつつ放出される硝酸を既知量のアリカリ溶液中に捕集して目標の放出量に到達した時点で反応を中止することにより、目的とする硝酸濃度比の亜化学量論的または化学量論的硝酸塩溶液を調製する。



(2)

特開平8-151204

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2

【特許請求の範囲】

【請求項1】 硝酸／金属性比（以下、硝酸濃度比と記す）が金属またはその複合陽イオン価数（以下、金属含有陽イオン価数という）に等しい化学量論的硝酸塩の溶液または固体、あるいはそれに過剰硝酸が加わった溶液または固体を出発物質として、硝酸濃度比が金属含有陽イオン価数より小さい亜化学量論的硝酸塩または化学量論的硝酸塩の溶液を得るために、出発物質の溶液または固体を水蒸気を含む気流中で加熱しつつ放出される硝酸を既知量のアリカリ溶液中に捕集して目標の放出量に到達した時点で反応を中止することにより、目的とする硝酸濃度比の亜化学量論的または化学量論的硝酸塩溶液を調製する方法。

【請求項2】 加熱温度が190°C以下である請求項1の亜化学量論的または化学量論的硝酸塩溶液調製方法。

【請求項3】 反応中止後の被加熱物質を80～99°Cに維持した状態で水を加えて固体をすべて溶解することによる請求項1の亜化学量論的または化学量論的硝酸塩溶液調製方法。

【請求項4】 硝酸濃度比が金属含有陽イオン価数の75～100%の範囲である請求項1の亜化学量論的または化学量論的硝酸塩溶液調製方法。

【請求項5】 該金属がウラン、トリウム、鉱ウラン元素の群から成る選ばれた1種またはそれ以上の核燃料物質である請求項1の亜化学量論的または化学量論的硝酸塩溶液調製方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は原子炉用セラミックス燃料粒子等の微小球状セラミックス粒子を調製する場合の出発物質として使用される核燃料物質等の亜化学量論的または化学量論的硝酸塩溶液の調製方法に関するものである。

【0002】

【従来の技術】 原子炉用セラミックス燃料粒子の分野において利用されているゾルゲル法による燃料ゲル粒子の製造工程では、出発物質溶液であるウラン等の燃料金属を含む亜化学量論的硝酸塩溶液を調製する場合、金属酸化物粉末を硝酸または化学量論的硝酸塩溶液に溶解するか、あるいは化学量論的硝酸塩溶液に有機物還元剤を加えて硝酸を分解・除去する方法を探っている。

【0003】

【発明が解決しようとする課題】 本発明の目的は、従来技術では不可欠の、作業員被曝の増大をもたらす放射性物質である燃料酸化物微粉末の取扱工程、あるいは有機物還元剤を酸化剤である硝酸塩溶液に添加する危険を伴う工程を経ずに、目的の出発物質溶液を調製する方法を提供することにある。

【0004】

【課題を解決するための手段とその作用】 本願発明者が

銳意研究の結果、目的とする課題解決のために採用した手段は次のとおりである。

【0005】 第1は、水蒸気を含む雰囲気中の加熱により、脱硝酸効率を高めたほか、放出ガスの主成分を窒素酸化物よりも硝酸の形にでき、目的の脱硝酸反応の終点を次のようにして正確に自動制御できるようにしたことである。すなわち、図1に例を示すような装置を用いて、担体ガス1をヒータ2で加熱した水3の中に導き水蒸気を含ませ、保温炉4を通して、ヒータ5で加熱した硝酸塩容器6内に導く。これにより放出した硝酸を担体ガスと共に冷却水を流していない冷却器7、流して冷却水を流している冷却器8を通して硝酸捕集用アルカリ溶液9の中に導く。この溶液中の当時のアルカリ量は放出させるべき硝酸と当量としておく。このアルカリ溶液のpHをpHメータ10につないだ記録調節計11で連続モニターリングし、放出硝酸とアルカリ溶液との中和反応の終点での急激なpH変化の信号により、ヒータ5による加熱を停止させると同時に、発生硝酸の系外放出を停止させるために冷却器7にも冷却水12を流すための音階切換弁13の操作を行う。

【0006】 第2は、反応終了後の容器6中の溶融塩状の被加熱物を室温まで冷却し固化させると、その固体の吸湿による体積膨張により容器破損が生ずるので、それを防ぐために水の沸点である100°C以下の高温に維持した状態で手動弁14を開き、水溜15の中水を加えて固体を水溶液に変えた後で冷却することである。

【0007】

【実施例】 実施例について本発明を具体的に説明する。ただし、本発明は実施例によって限定されるものではない。

【0008】

【実施例1】 図1の装置の試料（硝酸ウラニル溶液）の加熱ヒータとして油浴を用い、水蒸気発生器の95°Cの水の中にアルゴンを50ml/分の速度でバブルさせた（水蒸気+アルゴン）混合ガスを試料に供給、放出硝酸捕集用炭酸ナトリウム溶液を時々交換しながら放出硝酸量を調べる方法で、試料中のNO₃⁻／Uモル比の経時変化を調べた。反応前の試料は、U濃度が2.00mol/lでNO₃⁻／Uモル比が2.10である遊離硝酸含有硝酸ウラニル溶液60mlである。

【0009】 設定温度160°Cの油浴の加熱開始後約80分で試料温度が約110°Cになり硝酸の放出が始まり430分までの加熱の結果、NO₃⁻／Uモル比は1.86に達した。（捕集硝酸からの計算値は1.83で誤差の範囲で一致していた）。試料温度は290分以降147°Cであった。この間の試料温度と捕集硝酸から計算した試料のNO₃⁻／Uモル比とを、加熱開始後の時間に対して図2に示している。（図2には、アルゴンガスのみを供給した場合の結果も比較して示している。）

【0010】

(3)

特開平8-151204

4

3

【実施例2】実施例1と同様の手法で、油浴設定温度のみを195°Cに変えて、 NO_3^-/U モル比の経時変化を調べた。加熱開始後206分後に、 NO_3^-/U モル比は1.63に達した。(指差硝酸からの計算値は1.65で誤差の範囲で一致していた)。試料温度は130分以降180°Cであった。この間の試料温度と指差硝酸から計算した試料の NO_3^-/U モル比とを、加熱開始後の時間に対して図3に示している。(図3には、アルゴンガスのみを供給した場合の結果も比較して示している。)

【0011】

【実施例3】図1に示す装置を用いて、実施例2と同様の加熱前試料、加熱条件を適用し、 NO_3^-/U モル比の目標値を1.55として実験した。具体的には、放出硝酸ガス用アルカリ溶液には試料の NO_3^-/U モル比の最終値が1.55に達するまでの放出硝酸と当量の炭酸ナトリウムを含ませておき、その溶液のpHが4に達した時に、試料加熱ヒータからの電源断と冷却器7へ冷却水を供給する電磁切換弁13作動の信号を出すように設定しておいた。

【0012】試料温度は160分以降184°Cであった。252分後にpHが設定値以下となり、前記信号を発した。加熱終了後に試料温度が80°Cになった時に手動弁14を開いて所定の水を水槽15から試料容器内に供給した。内部の固体をすべて溶解するために最終的には95°Cに加熱した。この試料溶液の NO_3^-/U モル比は、目標値と誤差の範囲で一致する1.57であった。

【0013】

【発明の効果】従来の技術では、作業員被曝程度の増大*30

*を招く放射性微粉末を取り扱う工程、あるいは危険度の高い還元反応工程が必要であった。しかし、本発明の結果、これらの工程を不要としたほか、脱硝装置が目標どおり制御可能で、かつ、自動化の可能な亜化学量論的または化学量論的硝酸塩溶液の調製方法を実現させた。また、脱硝反応を水蒸気中で行うことにより、図2及び3に比較して示すように熱分解によるものより高い効率で進める方法を実現させた。

【図面の簡単な説明】

10 【図1】本発明の方法を実施するための装置の一例を示した図である。

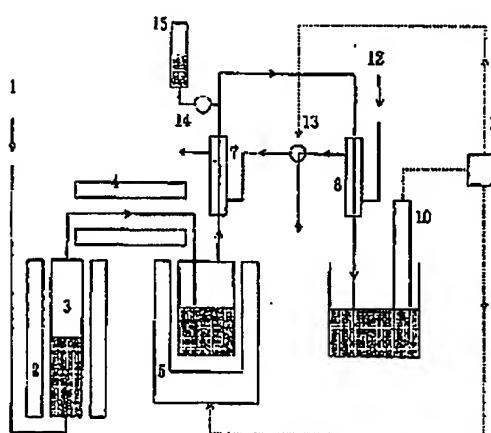
【図2】試料加熱ヒータとして160°C油浴を用いた実施例1の場合の試料温度と試料中の NO_3^-/U モル比の経時変化を、アルゴンガスのみを供給した場合と比較して示したグラフである。

【図3】試料加熱ヒータとして195°C油浴を用いた実施例2の場合の試料温度と試料中の NO_3^-/U モル比の経時変化を、アルゴンガスのみを供給した場合と比較して示したグラフである。

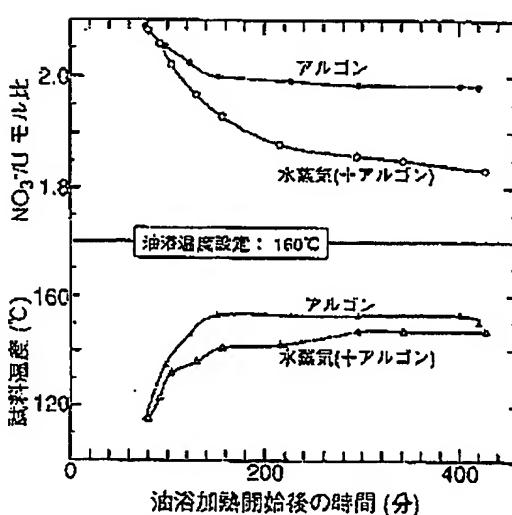
20 【符号の説明】

1: 惑体ガス発生器	2: ヒータ	3: 水蒸気
4: 保溫炉容器	5: ヒータ	6: 硝酸塩溶液
7: 冷却器	8: 冷却器	9: アルカリ溶液
10: pHメータ	11: 記録調節計	12: 冷却水
13: 電磁切換弁	14: 手動弁	15: 水槽

【図1】



【図2】



(4)

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【図3】

